

The Relative Migration Velocities
of the Ions of Silver Nitrate in Water,
Methyl Alcohol, Ethyl Alcohol
and Acetone, and in Binary Mixtures of
These Solvents, Together with the
Conductivity of Such Solutions.

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH THE REQUIREMENTS FOR THE DEGREE
OF DOCTOR OF PHILOSOPHY.

BY

CHARLES AUGUST ROUILLER

EASTON, PA. :
ESCHENBACH PRINTING COMPANY.
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PART I.

HISTORICAL SKETCH.

1. *Earlier Observations.*

Shortly after solutions began to be subjected to the action of the current from the voltaic pile, it was noticed that changes were produced at the poles. Carlisle¹ observed that in the decomposition of water alkali was formed at the cathode. This was later proved by Davy² to be due to the presence of saline impurities in the water. In the meantime it had been shown that this decomposition of salts, and the transference of the base to the negative pole and the acid to the positive electrode, was general, and Berzelius and Hissinger³ proposed their famous electrochemical theory.

About 30 years later Faraday⁴ performed some experiments to show that the passage of a current through a solution produces changes in concentration about the poles. Gmelin⁵ observed that when a solution of copper sulphate is electrolyzed between copper electrodes, it becomes colorless at the cathode, while the blue color about the anode increases in intensity. Pouillet⁶ found a similar change in concentration in a gold chloride solution.

In 1844 Daniel and Miller,⁷ continuing the earlier experi-

¹ Nicholson: Gilbert's Ann., 6, 340 (1800). Ostwald: "Elektrochemie," p. 130.

² Phil. Trans., 1807, p. 1. Ostwald's "Klassiker," No. 45.

³ Jour. d. Chem., 1, 115 (1803). Ostwald: "Elektrochemie," p. 317.

⁴ Pogg. Ann., 32, 401 (1834).

⁵ *Ibid.*, 44, 1 (1838).

⁶ Compt. rend., 20, 1544 (1845).

⁷ Phil. Trans., 1844, p. 1.

ments of Daniel,¹ made it clear that different ions do not travel with the same velocity. They electrolyzed solutions of various salts in a cell divided into compartments by porous membranes. Their experimental errors were so great, however, that they reached the erroneous conclusion that certain ions, such as those of copper and zinc, do not migrate at all.

Smee² performed many experiments which showed that the electric current causes changes in concentration, but he still advocated the Faraday theory of electrolysis.

2. Hittorf and His Method of Determining Transport Numbers.

The true explanation of these phenomena was finally offered by Hittorf,³ in 1853. He showed that the changes in concentration about the poles were due to the fact that the anions and cations traveled with different velocities, and that the amount of the change was a measure of the relative velocities of the two ions. In this way he determined the transport numbers for a very large number of salts.⁴ He devised various forms of apparatus, depending on the nature of the salt under investigation, but all were of the same general type—a vertical tube divided into sections by porous diaphragms. The cathode was placed in the upper and the anode in the lower cell.

Working with solutions of copper sulphate, he found that the current density and the temperature, between 4° and 21°, had no measurable effect on the transport number, but that the relative velocity of the copper ion increased with the dilution until it reached a constant, maximum value. Extending his investigations to other salts, he found that in some the transport number did not change with the dilution; others acted like copper sulphate, and in still others such as silver nitrate, the relative velocity of the cation decreased as the dilution increased.

The various forms of apparatus that he employed all have some objectionable features. The use of membranes, espe-

¹ Phil. Trans 1839, p. 97; 1840, p. 209.

² Phil. Mag., 17, 193 (1840); 25, 434 (1844).

³ Pogg. Ann., 89, 177 (1853). Ostwald's "Klassiker," No. 21.

⁴ Pogg. Ann., 89, 1 (1856); 103, 1 (1858); 106, 337 (1859). Ostwald's "Klassiker," Nos. 21 and 23.

cially, may be a serious source of error. Hittorf¹ himself recognized this nearly 50 years later, and repeated many of his experiments, using silk web instead of animal membranes. He found that when solutions of alkali salts are forced by endosmose through porous diaphragms, they are in no way changed, but solutions of the zinc and cadmium halides and many other electrolytes become more concentrated on the anode side, and the values obtained for the transport number of the cation are too low.

Hittorf's views met with extremely violent opposition, and for many years very little work was done in this field. Wiedemann,² in the course of his investigations on endosmose, measured the changes in concentration produced in various solutions by electrolysis. His apparatus consisted of two cylinders into which dipped glass tubes connected by rubber tubing.

Wieske³ determined a few transport numbers in an apparatus made of two bottles of known volume, connected near the top by a lateral tube. To separate the solutions after electrolysis, this tube was provided with a glass stop-cock.

Burgoin⁴ electrolyzed many organic acids and their salts, and studied quantitatively the products of decomposition. His apparatus consisted of two test-tubes, one inside the other, and communicating only by means of a small hole bored in the bottom of the smaller one.

Kirmis⁵ modified the Wiedemann apparatus by substituting glass for the rubber connections.

About this time F. Kohlrausch,⁶ as the result of a long series of conductivity measurements, was able to point out a close relationship between the velocities of ions and the conductivities of solutions. He showed that, in dilute solutions, under a given electromotive force, every ion moves through the liquid with a fixed velocity, dependent on its chemical nature but independent of the other ions. The conductivity, then, may be represented as the sum of two factors, related to each

¹ *Z. physik. Chem.*, **39**, 613 (1902); **43**, 239 (1903).

² *Pogg. Ann.*, **99**, 177 (1856).

³ *Ibid.*, **103**, 466 (1858).

⁴ *Ann. Chim. Phys.* [4], **14**, 157 (1868); [4], **21**, 264 (1870); [4], **22**, 361 (1871).

⁵ *Wied. Ann.*, **4**, 503 (1878).

⁶ *Ibid.*, **6**, 1, 145 (1879).

other as the transport numbers of anion and cation. If the constant maximum conductivity and the transport numbers are known, the absolute velocity of either ion can be easily calculated.

This did not at once lead to increased activity in the determination of transport numbers. Kuschel¹ and Lenz² investigated a few salts, using a slightly modified form of the Hittorf apparatus.

In 1888, wishing to test further Kohlrausch's law, Loeb and Nernst³ devised an apparatus for determining transport numbers, which did away entirely with porous diaphragms. It was essentially a Gay-Lussac burette provided near the top with a side tube for the reception of the cathode. Instead of the usual silver voltameter, they employed a galvanometer and Clark element in measuring the current. They determined the transport number of the silver ion in 8 salts and calculated its absolute velocity from their conductivity measurements. They found that the velocity, as calculated from the various salts, was constant to within the limits of experimental error.

The work of Chassy⁴ needs only to be mentioned. Kistiakowsky,⁵ in his determinations of transport numbers, used an extremely simple form of apparatus. It consisted merely of a vertical tube with a double bend near the top. His volt-meter is distinctive, the current being measured by determining volumetrically the amount of metal that had been dissolved from a silver anode.

Bein⁶ carried out quite an extensive investigation on the effect of membranes and of temperature on transport numbers. He found that porous clay plates had no effect on the relative velocities of the ions, but that fish bladder retarded the cation. With increase in temperature the ions tend to move with equal velocities.

Lusanna⁷ devised an apparatus of an entirely new form.

¹ Wied. Ann., **13**, 289 (1881).

² Mem. Acad. Imp. St. Petersburg., [7], **30** (1882).

³ Z. physik. Chem., **2**, 948 (1888).

⁴ Ann. Chim. Phys., [6], **21**, 241 (1890).

⁵ Z. physik. Chem., **6**, 97 (1890).

⁶ Wied. Ann., **46**, 29 (1892).

⁷ Att. Ist. Ven., [7], **3**, 1111 (1892); [7], **4**, 1568 (1893).

Three bulbs were connected by bent tubes in such a way as to form an S, and the whole apparatus, after being filled, was laid in the bath horizontally.

Rosenheim,¹ studying the composition of complex salts, subjected their solutions to electrolysis in two U-tubes connected by a rubber tube. Gordon² showed that the temperature coefficient of the transport numbers of cadmium sulphate and bromide is zero.

Schrader³ and Hopfgartner⁴ electrolyzed mixtures of salts and acids, to determine the relative velocities of different anions or cations.

Bein⁵ again took up the problem and carried out a very elaborate series of investigations. He studied the effects of temperature and of concentration on the transport numbers of a large series of salts. He also gave special attention to the determination of the influence of dividing membranes. He found that, in general, they retarded the cation. From experiments with clay, parchment paper, fish bladder and gold beater's skin, he showed that the greatest change in velocity was produced by animal membranes, while porous clay divisions are almost without influence. He describes 5 forms of apparatus, all very complex.

Starck,⁶ finding that the Hittorf apparatus with dividing membrane was not suitable for his purpose—the determination of the transport numbers for strong sulphuric acid—devised a simpler form, consisting of 3 U-tubes, connected by bent glass tubes.

In order to determine whether ternary electrolytes dissociate into complex ions, Noyes⁷ made very careful determinations of the transport numbers for potassium sulphate and barium chloride and nitrate, in 0.1 N and 0.2 N solutions. He concluded that, even in the more concentrated solutions of potassium sulphate and barium nitrate, there are practically

¹ Z. anorg. Chem., **11**, 225 (1896).

² Z. physik. Chem., **23**, 469 (1897).

³ Z. elek. Chem., **3**, 498 (1897).

⁴ Z. physik. Chem., **25**, 115 (1898).

⁵ *Ibid.*, **27**, 1 (1898); **28**, 439 (1899).

⁶ *Ibid.*, **29**, 385 (1899).

⁷ J. Am. Chem. Soc., **23**, 37 (1901).

no complex ions, while barium chloride solutions show evidence of the presence of considerable numbers of complex anions. In his investigation he used an apparatus consisting essentially of two U-tubes connected by rubber tubing.

Pfanhauser,¹ Rieger² and Bukschnewski³ made some determinations of transport numbers. Pfanhauser was investigating the properties of nickel ammonium sulphate and used the Hittorf apparatus. Rieger, to study the electrolytic decomposition products of various complex salts, devised a rather complicated cell which, however, made possible a complete separation of the cathode and anode solutions after electrolysis.

Notwithstanding all the work that had been done in this field, all forms of apparatus thus far devised possessed very objectionable features. The solutions around the electrodes were kept separated by porous diaphragms, or by differences in specific gravity, and it was impossible to effect complete separation. Some of the most serious defects were overcome by Mather,⁴ working with Jones, who used essentially an M-shaped tube divided into two equal compartments by a stop-cock of large bore. He made a few determinations of the transport numbers for silver nitrate and acetate and obtained satisfactory results.

Jahn⁵ and his pupils undertook an extensive study of the effect of dilution on transport numbers. Their apparatus was quite similar to that of Hopfgartner. An Erlenmeyer flask served as anode compartment, while the cathode dipped into the further limb of a U-tube connected with a flask near the top of a lateral tube. They investigated solutions ranging in dilution from $N/2$ to $N/300$, of hydrochloric and nitric acids, silver nitrate, copper and cadmium sulphates, and the halogen salts of the alkalis, the alkaline earths and cadmium. They found that, in general, the transport numbers for most of the salts they studied reached a maximum, constant value at comparatively low dilutions. The relative

¹ Z. elek. Chem., **7**, 698 (1901).

² *Ibid.*, **7**, 863 (1901).

³ Dissertation, Berlin, 1901.

⁴ Am. Chem. Journ., **26**, 473 (1901).

⁵ Z. physik. Chem., **37**, 673 (1901).

velocity of the silver ion in the nitrate was practically constant between $N/30$ and $N/214$. The copper ion in copper sulphate increased in velocity as compared with the anion, but reached its maximum relative speed in a $N/12$ solution. The transport numbers for the cadmium salts, as had already been shown some time previously by Hittorf, changed rapidly with the concentration.

Owing to the limited capacity of their apparatus, they were unable to work with any high degree of accuracy with solutions more dilute than $N/150$. Steele and Denison,¹ however, shortly afterwards devised an apparatus in which they could electrolyze unlimited amounts of solution. It was very similar to the form used by Noyes, but was connected at the top with a reservoir from which fresh solution could be supplied as the electrolyzed portions were drawn off at the bottom. They worked with calcium sulphate, nitrate and chloride, in solutions containing about 0.0045 gram-molecular weight of the salt to the liter. They found, from their transport number and conductivity measurements, that the velocity of the calcium ion was the same, whether determined from the chloride or the nitrate, while calcium and potassium chlorides gave concordant results for the velocity of the chlorine ion.

Among the more recent investigations may be mentioned those of Huybrecht² and Wolf.³ Both used the Hopfgartner-Jahn apparatus. Huybrecht studied magnesium sulphate and sulphuric acid. For this acid he found that the transport number of the hydrogen ion is constant for dilutions ranging between $N/8$ and $N/80$, and beyond $N/105$ it again has a constant, but somewhat higher value. Wolf obtained a negative temperature coefficient for the same ion in hydrochloric acid.

Noyes and Sammet⁴ made an accurate determination of the equivalent conductivity of hydrogen, by determining its transport number in hydrochloric acid. Using the same method with sulphuric acid, Tower⁵ finds that the relative velocity of

¹ J. Chem. Soc., **81**, 456 (1902).

² Dissertation, Berlin, 1901.

³ *Ibid.*, 1903.

⁴ J. Am. Chem. Soc., **24**, 944 (1903).

⁵ *Ibid.*, **26**, 1039 (1904).

the anion increases markedly with dilution, from 1 N to 0.02 N solution, and has a large temperature coefficient between 8°, 20° and 32°.

The application of Hittort's method to molten electrolytes by Lorenz and Fausti¹ is interesting. By the use of two porous clay cells, into which dipped carbon electrodes, they were able to show that in the electrolysis of a fused mixture of lead and potassium chlorides, the potassium migrates to the cathode and the lead to the anode, evidently as part of a complex anion.

Attention should be called to the papers of Stakelberg,² Burgess and Chapman³ and McBain⁴ on the determination of the relative velocities of complex ions which are partially dissociated into simpler ions.

3. The Direct Determination of Ionic Velocities.

The first direct determinations of the velocities of ions were made by Lodge⁵ in 1886. He dipped the two ends of a tube filled with dilute hydrochloric acid into vessels containing sulphuric acid and barium chloride, respectively, and passed a current through it from the salt solution to the acid. By noting the time, and the distance from the two ends of the tube of the point at which the barium and sulphate ions met, he was able to calculate their velocities. To prevent diffusion as much as possible, he substituted later, for the hydrochloric acid, a dilute solution of acetic acid in gelatin. In a second series of experiments he observed the actual progress of the chlorine ion by using silver sulphate as indicator and tracing the advance of the precipitate of silver chloride.

Whetham⁶ saw that Lodge's method had several objectionable features. The influence of the gelatin on the ionic velocities was entirely unknown, and no gelatin could be obtained so pure that it did not have a considerable conducting power of its own. In all methods based on the observation of the ad-

¹ Z. elek. Chem., **10**, 630 (1904).

² Z. physik. Chem., **23**, 493 (1897).

³ J. Chem. Soc., **85**, 1305 (1904).

⁴ Z. elek. Chem., **11**, 215, 961 (1905).

⁵ Brit. Assn. Rep., 1886, p. 389.

⁶ Phil. Trans. (A), 1893, p. 337.

vance of a precipitate, the precipitation of a part of the salt caused changes in concentration and, in aqueous solutions at least, mechanical disturbances. He therefore devised an apparatus in which the two solutions, which must have one ion in common while one of the other ions must possess a distinctive color, are held in a vertical tube, and the ionic velocity is determined by measuring the advance of the colored ion. To insure a uniform potential gradient, the two solutions must have about equal specific conductivities. Their densities must also be different in order to prevent mixing by diffusion. In a later series of experiments, Whetham¹ returns to the use of gelatin to prevent diffusion, and to precipitation methods to mark the advance of the ions. By making the quantity of indicator sufficiently small, the changes of concentration introduced by the last method become negligible. Lusanna² used Whetham's apparatus to study the effect of a magnetic field on ionic velocities.

Masson³ next took up the problem. He used Whetham's method, but placed his tube horizontally and used only colored solutions as indicators. He carefully studied the conditions which must govern the choice of an indicator solution. The colored ion must travel at a specifically slower rate than the ion whose advance it marks, and the indicator must be of such a nature that it will not react chemically with the gelatin or the salt under investigation, giving rise to new ions. Under such conditions, experiment shows that the boundary line between the colored and the colorless zones is very sharp, and Kohlrausch⁴ and Weber⁵ prove theoretically that there can be no mixture of the ions. In many cases, towards the end of the experiment, Masson noticed that cracks and flaws appeared in the gelatin, but this did not seem to affect the relative velocities of the moving boundaries.

A few years later, Steele⁶ devised a method which overcame many of the objectionable features of the older ones. The use

¹ Phil. Trans. (A), 1895, p. 607.

² Att. Ist. Ven., [7], 4, 1568 (1893).

³ Phil. Trans. (A), 192, 331 (1899).

⁴ Wied. Ann., 62, 209 (1897).

⁵ Sitz. Berl. Akad., 1897, p. 936.

⁶ Phil. Trans. (A), 198, 105 (1902).

of gelatin, as he notes, is impracticable, for the fall in potential is not uniform; the methods of Whetham and Masson are limited by the necessity of employing colored indicators, almost all of which give precipitates with the alkaline earths and the heavy metals. In his apparatus the solution under investigation is held in a vertical tube, between columns of gelatin containing the indicator in solution. The progress of the bounding layer can be easily followed, if the two solutions have slightly different refractive powers. The choice of indicators is thus largely increased. Measurements with salts like magnesium sulphate in both gelatin and water showed that the ionic velocities were affected by the gelatin, but with the alkali chlorides and bromides the velocities seem to be independent of the medium through which the ions travel.

Steele's values did not agree as well as could be desired with the transport numbers determined by Hittorf's method, and Abegg and Gauss¹ suggested that it might be due to endosmose. Modifying Steele's apparatus in such a way that they could measure the amount of solution forced through the gelatin and thus make the proper correction for it, they obtained, with potassium chloride, values agreeing very closely with those of Hittorf.

Denison² has extended this investigation to various other salts. He reaches the following conclusions :

1. In water, when correction is made for endosmose, the transport numbers for the simple sodium and potassium salts, determined in this way, agree with Hittorf's values.
2. For salts which form complex ions, or hydrolyze, the two sets of values do not agree but show parallelism.
3. Solid gelatin decreases the velocity of the cation. High concentration seems to have the same effect. Liquid gelatin does not influence the ionic velocities.

In a very recent paper, Denison and Steele³ describe an apparatus and method in which they have entirely discarded the use of gelatin. The solution under investigation is inclosed between layers of aqueous solutions of the indicators, usually

¹ Z. physik. Chem., **40**, 737 (1902).

² *Ibid.*, **44**, 575 (1903).

³ Phil. Trans. (A), 1906, p. 449.

lithium chloride for the cation and sodium formate, acetate or benzene sulphonate for the anion. The lead cathode is covered with lead peroxide and surrounded with dilute acetic acid. The anode is of cadmium amalgam. A little lithium hydroxide in the anode chamber retains the hydrogen ions formed by the hydrolysis of the cadmium chloride. With this apparatus they determined the transport numbers for the chlorides of the alkalies and alkaline earths, the nitrate, sulphate, chlorate, bromate, bromide and iodide of potassium, the alkali hydroxides, and hydrochloric, nitric and sulphuric acids in 0.1 N and 0.02 N solutions, and have obtained values agreeing very satisfactorily with those obtained by Hittorf's method. They claim for their method just as great accuracy, and a very large saving in time and labor.

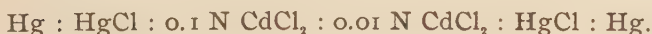
4. *Other Methods for Determining the Migration Velocities of Ions.*

Various other methods for determining migration velocities have from time to time been proposed.

Kummel,¹ who determined the transport numbers of the halides and sulphates of zinc and cadmium by the Hittorf method, also measured the electromotive forces of concentration elements of the type



and



As shown by Nernst,² from the ratio of the electromotive forces of two such elements, the transport numbers for the soluble salt can easily be calculated. Kummel obtained values for zinc and cadmium chlorides and cadmium sulphate that agreed very well with those found by the Hittorf method.

Kendrick³ determined the transport number of the anion of sulphuric acid, containing from 1.4 to 55 per cent of H_2SO_4 , by measuring the electromotive forces of 3 types of concentration elements:

¹ Wied. Ann., **64**, 655 (1898).

² Z. physik. Chem., **4**, 129 (1889).

³ Z. elek. Chem., **7**, 52 (1900).

Pb : dil. H_2SO_4 : conc. H_2SO_4 : Pb ;

H_2 : dil. H_2SO_4 : conc. H_2SO_4 : H_2 ;

PbO_2 : dil. H_2SO_4 : conc. H_2SO_4 : PbO_2 .

McIntosh¹ shows that the ratio of the electromotive forces of concentration elements, with and without diffusion, is equal to the transport number, and by this means he determined the transference number of hydrogen. He used cells of the type—

H_2 : HCl : HgCl : HCl : H_2 —without diffusion ;

H_2 : HCl : HCl : H_2 —with diffusion.

The values obtained from duplicate experiments differ rather widely, and McIntosh concludes that the method is not applicable to gas cells, but it has been pointed out that the mean of his determinations does not differ more from the value calculated from Kohlrausch's conductivity measurements, than do the results of the different investigators using Hittorf's method.

When the solution of a salt, like copper sulphate, is electrolyzed, the process will be normal so long as the current density is kept below a certain point, but as soon as this critical point is passed, secondary processes set in and gas is evolved at the cathode. Weber² offered a possible explanation. At the critical density the copper ions, which, under a given electromotive force move with a fixed velocity, are just able to carry over all the positive electricity, and if this critical density is known, the absolute velocity of the ions can be calculated. Weber electrolyzed various solutions, gradually increasing the current density till a sudden rise in resistance gave evidence of polarization. This, he assumed, showed that the critical density had been reached. Experiments with copper and cadmium sulphates and zinc nitrate, gave results which agreed quite well with those of Kohlrausch.

Sheldon and Downing,³ using solutions of copper sulphate, increased the current density by gradually withdrawing the cathode, a cylinder of known diameter, from the solution. As soon as the critical density was reached, the copper ceased

¹ J. Phys. Chem., **2**, 273 (1898).

² Z. physik. Chem., **4**, 182 (1889).

³ Phys. Rev., **1**, 51 (1894).

to be deposited in bright, metallic form, and the line of demarcation between the bright and the dark deposit was found to be quite sharp. They were thus able to determine the area of the cathode at the critical density, and from this the current density itself and the velocity of the copper ion.

5. *Ionic Velocities in Non-aqueous Solvents.*

Until within the last 3 years, very few determinations of ionic velocities had been made in solvents other than water. Hittorf, in his extensive investigation of transport numbers, electrolyzed a few solutions in ethyl and amyl alcohols. Lenz has recorded some measurements that he made with cadmium iodide in mixtures of water and alcohol.

Cattaneo¹ determined the effect of glycerol, methyl, ethyl and amyl alcohols, and mixtures of ethyl alcohol, chloroform and ether, on the transport number of the chlorine ion in hydrochloric acid. He found in all cases that the influence of the solvent was very slight. Campetti² measured the transport numbers for lithium chloride and silver nitrate in ethyl alcohol. Whetham determined directly the velocity of the cobalt ion in alcoholic solutions of cobalt chloride and nitrate. Mather worked with silver nitrate in mixtures of ethyl alcohol and water.

Schlundt³ carried out some experiments with silver nitrate in pyridine and acetonitrile. Silver nitrate has a great "affinity" for these two liquids, and crystallizes from pyridine with 2 and 3 molecules of the solvent. As Schlundt expected, the relative velocity of the silver ion increases with the dilution. This is analogous to the phenomena observed in aqueous solution, with those salts which come out of solution with water of crystallization; the transport number of the cation almost always increases with the dilution.

Roth⁴ gives some unpublished determinations of transport numbers made by Hornbostel and Goldberger, in mixtures of ethyl alcohol and water, containing from 10 to 40 per cent of

¹ Rend. Acc. Lincei [5], **5**, 207 (2 sem., 1897); [5], **6**, 279 (1 sem., 1898).

² Il Nuovo Cimento, **35**, 225 (1894). Ref., Z. physik. Chem., **16**, 165 (1895).

³ J. Phys. Chem., **6**, 159 (1902).

⁴ Z. physik. Chem., **42**, 219 (1903).

alcohol. Eisenstein¹ also worked along this line. From sodium chloride, the transport number of the chlorine ion increases with the amount of alcohol, but is unaffected by dilution. Goldberger's results with barium chloride are given below: v = the number of liters of solution containing a gram-molecular weight of the salt; a = the transport number of the anion:

	Percentage of Alcohol.					
	0 per cent.	10 per cent.	20 per cent.	25 per cent.	30 per cent.	40 per cent.
v .	a .	a .	a .	a .	a .	a .
30	0.543	0.531	0.540	0.549		0.536
60	0.548	0.536	0.543	0.551	0.545	0.536
90	0.553	0.545	0.547	0.550		0.536
120	0.554	0.546				0.536

The addition of small quantities of alcohol to the aqueous solution produces a lowering of the transport number, but as the proportion of alcohol is increased the relative velocity of the chlorine ion also increases, and reaches a maximum value in the mixture containing 25 per cent of alcohol. A further addition of alcohol produces a steady decrease. The transport number also increases with the dilution.

The first systematic study of ionic velocities in non-aqueous solvents was made by Carrara.² He used three pieces of apparatus, two of which had been devised by earlier investigators, Hittorf and Loeb and Nernst, while the third, he claims, is a new form, although it is very similar to that of Jones and Mather. He determined the transport numbers for some 20 salts of copper, cadmium and lithium, in methyl alcohol and, comparing them with the corresponding values for aqueous solutions, reached the conclusion that the relative velocities of the ions of an electrolyte tend toward the same value, independent of the solvent.

Dempwolf,³ shortly afterwards, also determined the transport numbers for a large number of salts in methyl alcohol, and found that the oxymethyl ion, OCH_3 , of sodium methylate, has a velocity about equal to that of the chlorine ion.

¹ Dissertation, Berlin, 1902.

² Gazz. chim. ital., **33**, I., 241 (1903).

³ Physik. Z., **5**, 637 (1904).

Jones and Bassett,¹ with the same apparatus that has been used in the present investigation, measured the relative velocity of the anion of silver nitrate at 0° and 25° in water, methyl and ethyl alcohol, and mixtures of water and methyl alcohol. They draw the following conclusions from their work :

“ The difference in the relative velocities observed in the pure solvents at 0° and 25°, become less as the temperature rises, and the velocities, therefore, tend toward equality. This has already been observed for pure solvents, but it does not hold in the case of mixed solvents.

“ The relative velocities are largely dependent on the nature of the solvent.

“ In mixed solvents the relative velocities are dependent on both the temperature and the composition of the mixture.”

One of the most interesting investigations ever carried out in this field is that of Franklin and Cady,² on the determination of transport numbers of various salts in liquid ammonia. With considerable ingenuity they so modified Steele's apparatus that they were able to use it, satisfactorily, with such a low-boiling solvent as ammonia. The lower part of the tube was closed by a thread of mercury. In determinations of the velocities of cations, this mercury thread served as anode, and the mercury ions thus formed as the indicators. For anions, picric acid was generally employed as indicator. They found that for sodium and potassium nitrates, and sodium chloride and bromide, the ionic velocities are independent of the concentration. As was to be expected from the dielectric constant and association factor of liquid ammonia, the results of their work showed that the unusually high conductivities of solutions in this liquid, observed by Cady,³ were due, not to a large dissociation, but to the high velocities of the ions in this medium. From their determinations of transport numbers and Cady's conductivity measurements, they demonstrate that the conductivity of completely dissociated electrolytes in liquid

¹ *Am. Chem. Journ.*, **32**, 409 (1904).

² *J. Am. Chem. Soc.*, **26**, 499 (1904).

³ *J. Phys. Chem.*, **1**, 707 (1897).

ammonia is 2.5 to 3 times as high as the corresponding values in water.

Equally interesting is the very recent work of Steele, McIntosh and Archibald¹ on the properties of the liquid halogen acids. They find that such compounds as ether, acetone, substituted ammonium salts and ketones, in general, dissolved in liquid hydrobromic acid, conduct the current very well. After satisfying themselves, by measuring the amount of hydrogen liberated during electrolysis, that these solutions obey Faraday's law, they determined the transport number of the cation at two dilutions. They conclude that liquid hydrobromic acid forms addition products with the solute, and that these dissociate into complex cations and simple bromine anions.

PART II.

EXPERIMENTAL.

Object of This Investigation.

This work is a direct continuation of the investigation carried out in this university two years ago by Jones and Bassett.² They wished, if possible, to trace a connection between the phenomena of minimum conductivity, first observed by Zelinsky and Krapivin³ and later extensively studied by Jones and Lindsay,⁴ which solutions in certain mixtures of alcohol and water exhibit. Jones⁵ and his students have extended the investigation of this problem to mixtures of other solvents, including acetone, and have obtained interesting results. It was, therefore, thought desirable to extend also the work of Jones and Bassett. The conductivity of silver nitrate and the transport number of its anion in binary mixtures of water, methyl alcohol, ethyl alcohol and acetone, have been determined at two temperatures, 0° and 25°. In their determination of transport numbers, Jones and Bassett worked with 0.1 N solutions, but, owing to the limited solubility of silver nitrate in acetone, and to the desira-

¹ Phil. Trans. (A), 1905, p. 99.

² Am. Chem. Journ., **32**, 409 (1904).

³ Z. physik. Chem., **21**, 35 (1896).

⁴ Am. Chem. Journ., **28**, 329 (1902).

⁵ *Ibid.*, **32**, 521 (1904); **34**, 481 (1905).

bility of having comparable values throughout, all measurements in this work have been made with 0.02 N solutions.

Solvents.

Water.—The water used in preparing the solutions was purified essentially by the method of Jones and Mackay.¹ Ordinary distilled water was twice redistilled from an acidified solution of potassium bichromate, and the steam from the second distillation passed through a boiling solution of barium hydroxide. It had, at 0°, a conductivity of about 1.0×10^{-6} .

Methyl Alcohol.—The purest obtainable product was boiled 1 to 2 days with lime, distilled and allowed to stand over anhydrous copper sulphate till needed. All distillations were made through a Singer fractionating head and a block-tin condenser, and the liquid was protected during distillation from the moisture in the air by means of a soda lime U-tube. To prevent any possibility of soda lime dust being drawn back into the liquid, the end of the tube nearest the bottle was covered with filter paper. The first and last portions of the distillate were always discarded. The mean conductivity at 0° = 0.8×10^{-6} .

Ethyl Alcohol.—The best commercial article was treated in the same manner as the methyl alcohol. Its conductivity at 0° was about 2.0×10^{-7} .

Acetone.—The acetone was allowed to stand over fused calcium chloride before using. Conductivity at 0° = 1.0×10^{-6} .

Mixed Solvents.—The mixture obtained by adding n cc. of Solvent *A* to 100— n cc. of Solvent *B* was designated as an “ n per cent *A*—(100— n) per cent *B* mixture.” This method of preparing mixed solvents was deemed preferable to the more common method of diluting n cc. of Solvent *A* to 100 cc. with Solvent *B*. In the latter case it is always necessary to state which solvent is used as diluent, and the mixture must always be allowed to cool down to the temperature of the unmixed solvents before the final dilution to the mark on the measuring flask can be effected.

¹ Am. Chem. Journ., 19, 83 (1897).

I. Conductivity.

Apparatus.—In making conductivity measurements, the usual Kohlrausch method, with Wheatstone bridge, induction coil and telephone receiver, was used. The bridge wire was of "manganin." The resistance coils were made by Leeds, of Philadelphia, and were calibrated to within 0.04 of 1 per cent.

The conductivity cells were of the type devised by Jones and Bingham¹ for use with volatile solvents, which, like acetone, attack rubber and wax. They differ from the simple Arrhenius cells in that the cup is closed by a ground glass stopper, into which are sealed with glass the tubes that carry the electrodes.

The electrodes were carefully cleansed with chromic acid and covered with platinum black, by electrolyzing a dilute solution of platinic chloride. All absorbed chlorine was removed with sodium hydroxide and the plates were washed with dilute hydrochloric acid and distilled water, dried and heated to redness in the flame of a blast-lamp. Electrodes thus treated gave a good tone minimum, did not appreciably absorb salts from their solutions and showed no tendency to cause the rapid oxidation of alcohol to acetic acid. When not in use the cells were filled with distilled water. Solutions were never allowed to stand in them longer than was necessary.

The 0° bath was of the form commonly used in this laboratory. A tin pail was filled with finely crushed ice and water and the cells were then packed into the ice as tightly as possible. The pail was placed into a larger, indurated filter bucket and the intervening space filled with finely crushed ice and water. Such a bath will maintain a temperature to within 0°.1 of 0° for hours. The 25° bath was a galvanized iron tub, lined on the outside with asbestos. The water in it was kept at a uniform temperature by means of a stirrer driven by a small hot-air motor, and could easily be kept to within 0°.1 of any desired temperature. The thermometers were graduated to 0°.1 and standardized. The burettes and measuring flasks

¹ Am. Chem. Journ., 34, 481 (1905).

were all carefully calibrated by the method of Morse and Blalock.¹

Preparation of Solutions.—The silver nitrate used in this work was obtained from Kahlbaum, and was perfectly neutral. It was finely pulverized, dried for several hours at 100° – 105° and kept in a desiccator in the dark. Somewhat more of the salt than was necessary to prepare a 0.02 N solution was weighed into the solvent, and the exact concentration was determined by titration with a 0.04 N solution of ammonium sulphocyanate, with ferric ammonium sulphate as indicator. The sulphocyanate solution was standardized against a 0.04 N solution of silver nitrate, and weighed quantities of thoroughly dried potassium chloride, which had been especially purified in this laboratory for use in conductivity work. The solution whose conductivity was to be measured was then made exactly 0.02 N by the addition of the proper amount of solvent. From this mother-solution the other solutions were prepared by successive dilution. The N/800 and N/1200 solutions were prepared from the N/400.

Conductivity Measurements.—In measuring the conductivity of a solution, readings were always made with three different resistances, and the values given are the mean. Before using, the cells and electrodes were carefully dried and rinsed out with the solution whose conductivity was to be measured. The cell constants were determined with 0.02 N and 0.004 N solutions of pure potassium chloride. The molecular conductivity of the former was taken as 129.7 at 25° .

In the following tables, under v is given the concentration, expressed in number of liters of the solution containing a gram-molecular weight of the salt; under $\mu_v 0^{\circ}$, the molecular conductivity at 0° ; and under $\mu_v 25^{\circ}$, the molecular conductivity at 25° .

The temperature coefficients are obtained by dividing the increase in conductivity per degree by the conductivity at 0° .

The values for the molecular conductivities in water and methyl and ethyl alcohols are obtained, by interpolation, from

¹ Am. Chem. Journ., 16, 479 (1894).

the measurements of Jones and Bassett, and the temperature coefficients are calculated from those interpolated values.

Table I.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	38.97	78.79
100	40.91	81.82
200	42.36	85.70
400	41.65	85.00
800	43.24	88.24
1200	45.01	91.71

Conductivity of solvent at 0° = 1.15×10^{-6} .

Table II.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 15°.
50	31.31	62.97
100	31.72	64.34
200	33.00	67.69
400	33.74	68.50
800	34.32	71.12
1200	34.57	70.60

Conductivity of solvent at 0° = 1.66×10^{-6} .

Table III.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	30.79	53.04
100	34.59	60.05
200	36.49	63.81
400	38.75	68.34
800	40.35	70.63
1200	40.26	71.28

Conductivity of solvent at 0° = 2.06×10^{-6} .

Table IV.—*Molecular Conductivity of Silver Nitrate in Acetone.*

v .	μ_v 0°.	μ_v 25°.
125	7.93	10.08
200	8.18	10.36
400	8.58	11.57
800	9.64	12.08
1200	10.54	13.11

Conductivity of solvent at 0° = 1.0×10^{-6} .

Table V.—*Molecular Conductivity of Silver Nitrate in Water, Acetone, and Mixtures of These Solvents at 0°.*

v .	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	63.11	38.97	31.31	30.79	. .
100	63.71	40.91	31.72	34.59	. .
200	66.51	42.36	33.00	36.49	8.18
400	70.19	41.65	33.74	38.75	8.58
800	70.94	43.24	34.32	40.35	9.64
1200	70.65	45.01	34.57	40.26	10.54

Table VI.—*Molecular Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents at 25°.*

v .	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	111.62	78.79	62.97	53.04	. .
100	116.82	81.82	64.34	60.05	. .
200	121.16	85.70	67.69	63.81	10.36
400	125.27	85.00	68.50	68.34	11.57
800	125.73	88.24	71.12	70.63	12.08
1200	125.43	91.71	70.60	71.28	13.11

Table VII.—*Temperature Coefficients of Conductivity of Silver Nitrate in Water, Acetone and Mixtures of These Solvents, 0°–25°.*

v .	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0307	0.0409	0.0404	0.0289	. .
100	0.0334	0.0400	0.0411	0.0294	. .
200	0.0329	0.0409	0.0430	0.0299	0.0107
400	0.0314	0.0416	0.0424	0.0305	0.0139
800	0.0309	0.0416	0.0429	0.0300	0.0101
1200	0.0310	0.0415	0.0417	0.0308	0.0097

The values in Tables I. to VI. are plotted as curves in Figs. I. and II., the abscissae representing the different percentages of acetone, and the ordinates the molecular conductivities. It

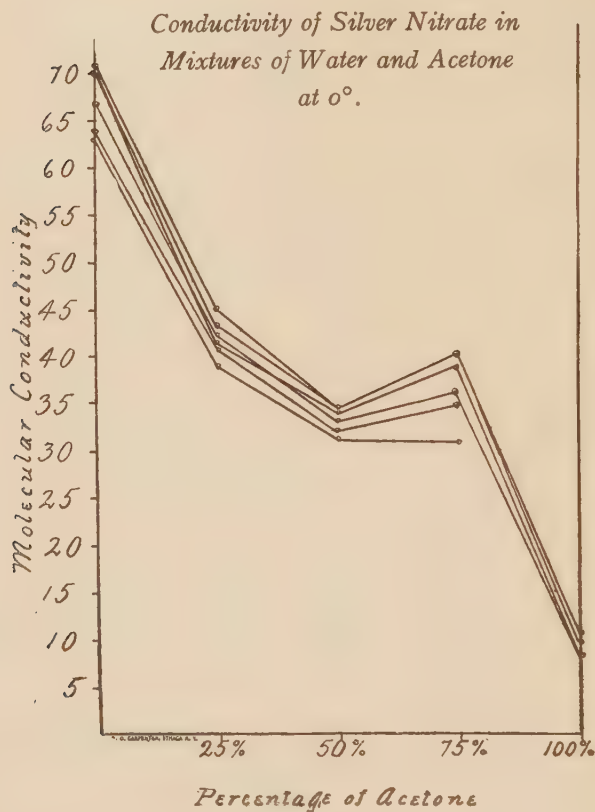


Fig. I.

will be seen that at 0°, for all dilutions but the lowest investigated, 0.02 N, there is a pronounced point of inflection that appears in the 75 per cent acetone mixture. At 25° it has al-

most disappeared, but still manifests itself at the higher dilutions. The curves are almost identical in form with those obtained by Jones and Bingham¹ for calcium nitrate, in mixtures of the same solvents.

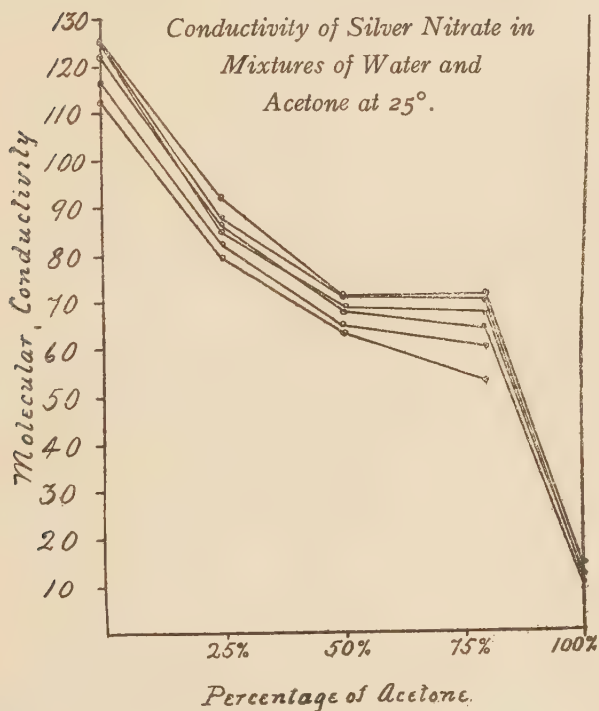


Fig. II.

Table VII. shows that the temperature coefficients increase with the proportion of acetone up to the 50 per cent mixture, but a further increase in the proportion of acetone produces a

¹ Am. Chem. Journ., 34, 481 (1905).

rapid fall in the values for the temperature coefficients. With increase in concentration, the maximum value tends to shift to the 25 per cent acetone mixture. These results are also almost identical with those obtained by Jones and Bingham with calcium nitrate.

Table VIII.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Ethyl Alcohol Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	32.39	45.69
100	38.01	54.09
200	44.94	64.40
400	47.09	67.72
800	50.45	72.85
1200	51.66	74.88

Conductivity of solvent at 0° = 7.4×10^{-7} .

Table IX.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Ethyl Alcohol Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	24.06	35.24
100	29.04	42.39
200	32.17	47.29
400	35.93	53.04
800	39.22	58.10
1200	40.06	59.68

Conductivity of solvent at 0° = 3.1×10^{-7} .

Table X.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent. Methyl Alcohol—75 Per Cent Ethyl Alcohol Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	17.45	26.54
100	20.78	31.89
200	23.40	36.41
400	26.45	41.32
800	28.38	44.71
1200	28.91	46.03

Conductivity of solvent at 0° = 3.8×10^{-7} .

Table XI.—*Molecular Conductivity of Silver Nitrate in Methyl and Ethyl Alcohols, and Mixtures of These Solvents at 0°.*

v.	Percentage of Ethyl Alcohol.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent. (Bassett.)
50	41.10	32.39	24.06	17.45	11.79
100	46.73	38.01	29.04	20.78	13.61
200	52.49	44.94	32.17	23.40	15.61
400	57.89	47.09	35.93	26.45	17.64
800	. .	50.45	39.22	28.38	. .
1200	. .	51.66	40.06	28.91	. .

Table XII.—*Molecular Conductivity of Silver Nitrate in Methyl and Ethyl Alcohols, and Mixtures of These Solvents at 25°.*

v.	Percentage of Ethyl Alcohol.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent. (Bassett.)
50	55.80	45.69	35.24	26.54	17.75
100	64.80	54.09	42.39	31.89	21.05
200	72.81	64.40	47.29	36.41	24.52
400	82.18	67.72	53.04	41.32	27.50
800	. .	72.85	58.10	44.71	. .
1200	. .	74.88	59.68	46.03	

Table XIII.—*Temperature Coefficients of Conductivity of Silver Nitrate in Methyl and Ethyl Alcohol and Mixtures of These Solvents, 0°–25°.*

v.	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0143	0.0164	0.0186	0.0208	0.0202
100	0.0155	0.0169	0.0184	0.0214	0.0189
200	0.0155	0.0173	0.0188	0.0222	0.0203
400	0.0168	0.0175	0.0190	0.0225	0.0224
800	. .	0.0178	0.0192	0.0230	. .
1200	. .	0.0180	0.0196	0.0237	. .

Tables VIII. to XII. (Figs. III. and IV.) show that there is no trace of either a maximum or minimum, the curves being

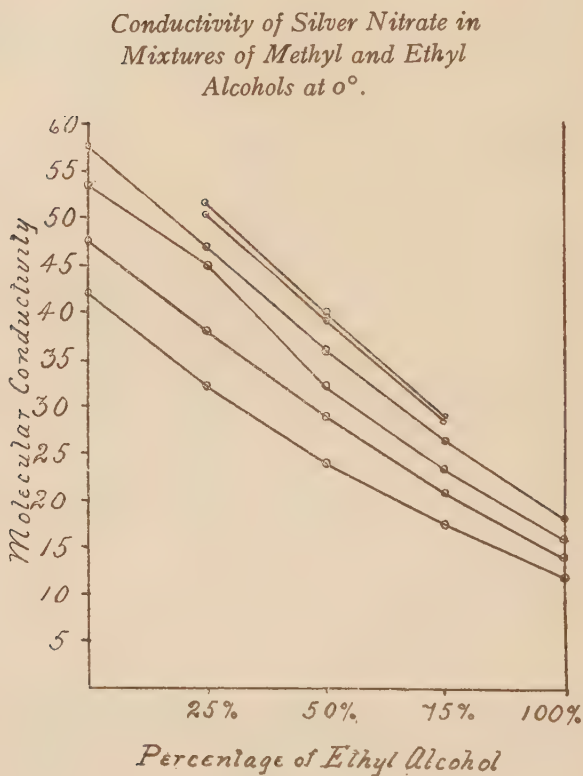


Fig. III.

straight lines to within the limits of experimental error. The temperature coefficients (Table XIII.) increase regularly with

the proportion of ethyl alcohol up to the 75 per cent mixture, and then remain practically constant, showing a slight tendency to drop.

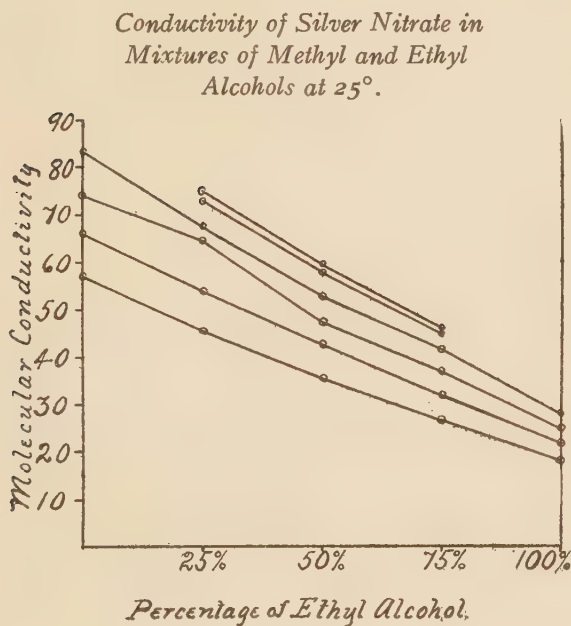


Fig. IV.

Table XIV.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	40.45	53.81
100	46.36	64.24
200	55.60	73.65
400	63.98	83.08
800	65.62	92.69
1200	71.85	96.70

Conductivity of solvent at 0° = 1.3×10^{-6} .

Table XV.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture.

<i>v.</i>	μv 0°.	μv 25°.
50	38.46	45.94
100	48.31	61.69
200	58.22	68.61
400	67.87	83.88
800	77.83	100.90
1200	81.57	100.40

Conductivity of solvent at 0° = 1.36×10^{-6} .

Table XVI.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Methyl Alcohol—75 Per Cent Acetone Mixture.

<i>v.</i>	μv 0°.	μv 25°.
50	25.49	28.40
100	33.67	37.78
200	42.42	47.00
400	51.50	59.87
800	63.19	75.12
1200	66.71	78.19

Table XVII.—Molecular Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents at 0°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	41.10	40.45	38.46	25.49	. .
100	46.73	46.36	48.31	33.67	. .
200	52.49	55.60	58.22	42.42	8.18
400	57.89	63.98	67.87	51.50	8.58
800	. .	65.62	77.83	63.19	9.64
1200	. .	71.85	81.57	66.71	10.54

Table XVIII.—*Molecular Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents at 25°.*

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	55.80	53.81	45.94	28.40	. .
100	64.80	64.24	61.69	37.78	. .
200	72.81	73.65	68.61	47.00	10.36
400	72.18	83.08	83.88	59.87	11.57
800	. .	92.69	100.90	75.12	12.08
1200	. .	96.70	100.40	78.19	13.11

Table XIX.—*Temperature Coefficients of Conductivity of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents, 0°–25°.*

<i>v.</i>	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0143	0.0132	0.0078	0.0046	. .
100	0.0155	0.0154	0.0119	0.0049	. .
200	0.0155	0.0130	0.0071	0.0068	0.0107
400	0.0168	0.0119	0.0119	0.0065	0.0139
800	. .	0.0165	0.0119	0.0076	0.0101
1200	. .	0.0138	0.0092	0.0069	0.0097

A study of Tables XIV. to XVIII. (Figs. V. and VI.) shows that at 0°, at the higher dilutions, silver nitrate in mixtures of methyl alcohol and acetone gives a maximum that almost disappears at 25°, although still evident in the more dilute solutions. The maximum appears in the 50 per cent

mixture. Here again the results are very similar to those found for calcium nitrate by Jones and Bingham, although silver nitrate does not, like the calcium salt, show, within the

*Conductivity of Silver Nitrate in
Mixtures of Methyl Alcohol and
Acetone at 0°.*

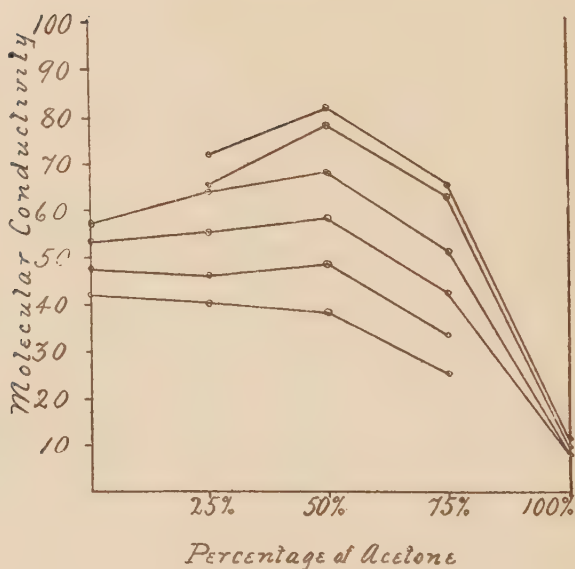


Fig. V.

limits of the dilutions investigated, any maximum in the 25 per cent acetone mixture.

The temperature coefficients (Table XIX.) exhibit a pro-

nounced maximum in the 75 per cent acetone mixture. This applies equally well to calcium nitrate.

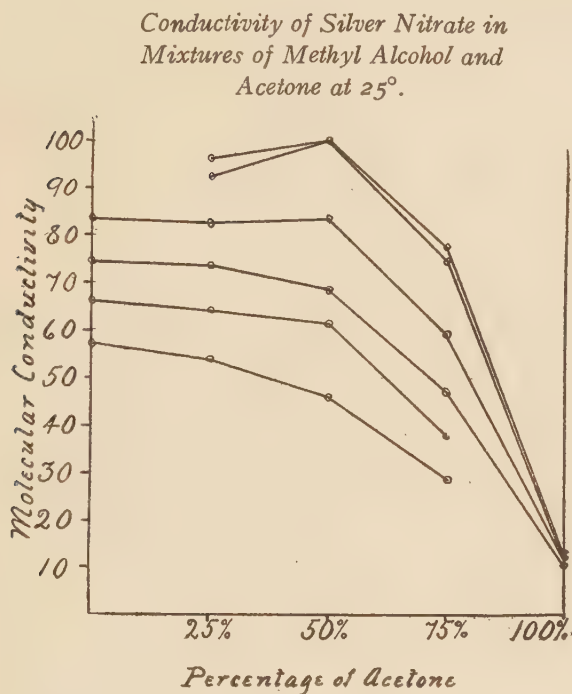


Fig. VI.

Table XX.—Molecular Conductivity of Silver Nitrate in a 75 Per Cent Ethyl Alcohol—25 Per Cent Acetone Mixture.

<i>v.</i>	μ_v 0°.	μ_v 25°.
50	15.86	22.39
100	19.90	28.38
200	25.06	33.64
400	27.40	39.82
800	31.51	46.30
1200	32.85	49.04

Conductivity of solvent at 0° = 2.4×10^{-7} .

Table XXI.—Molecular Conductivity of Silver Nitrate in a 50 Per Cent Ethyl Alcohol—50 Per Cent Acetone Mixture.

<i>v.</i>	μv 0°.	μv 25°.
50	16.91	21.42
100	22.13	28.12
200	25.72	33.64
400	33.55	43.49
800	40.51	53.51
1200	43.90	58.69

Conductivity of solvent at 0° = 4.6×10^{-7} .

Table XXII.—Molecular Conductivity of Silver Nitrate in a 25 Per Cent Ethyl Alcohol—75 Per Cent Acetone Mixture.

<i>v.</i>	μv 0°.	μv 25°.
50	13.38	16.36
100	17.42	23.06
200	22.20	27.60
400	29.80	.
800	37.84	45.80
1200	43.76	55.33

Conductivity of solvent at 0° = 4.4×10^{-7} .

Table XXIII.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents at 0°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	11.79	15.86	16.91	13.38	. .
100	13.61	19.90	22.13	17.42	. .
200	15.61	25.06	25.72	22.20	8.18
400	17.64	27.40	33.55	29.80	8.58
800	. .	31.51	40.51	37.84	9.64
1200	. .	32.85	43.90	43.76	10.54

Table XXIV.—Molecular Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents at 25°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent. (Bassett.)	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	17.75	22.39	21.42	16.36	. .
100	21.05	28.38	28.12	23.06	.
200	24.52	33.64	33.64	27.60	10.36
400	27.50	39.82	43.49	. .	11.57
800	. .	46.30	53.51	45.80	12.08
1200	. .	49.04	58.69	55.33	13.11

Table XXV.—Temperature Coefficients of Conductivity of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents, 0°–25°.

<i>v.</i>	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
50	0.0202	0.0165	0.0107	0.0089	.
100	0.0189	0.0170	0.0108	0.0130	. .
200	0.0203	0.0137	0.0123	0.0097	0.0107
400	0.0224	0.0181	0.0118	. .	0.0139
800	. .	0.0188	0.0128	0.0084	0.0101
1200	. .	0.0197	0.0134	0.0106	0.0097

The similarity of the curves (Figs. VII. and VIII.) plotted from the values given in Tables XX. to XXIV., to the corresponding curves obtained by Jones and Bingham for calcium nitrate, is even more striking than in the case of the methyl alcohol and acetone mixtures. A pronounced minimum manifests itself at both 0° and 25°, appearing in the 25 per cent acetone mixture in the more concentrated solutions, and shifting, with increase in dilution, through the 50 per cent to the 75 per cent mixture.

As with calcium nitrate, the temperature coefficients (Table XXV.) show a minimum in the 75 per cent mixture.

In view of the great similarity in conductivity phenomena

exhibited by silver and calcium nitrates, in mixtures of water and of methyl and ethyl alcohols with acetone, it is interesting to know whether this is also true of solutions of the two salts in mixtures of water with the alcohols. By comparing the

Conductivity of Silver Nitrate in Mixtures of Ethyl Alcohol and Acetone at 0°.

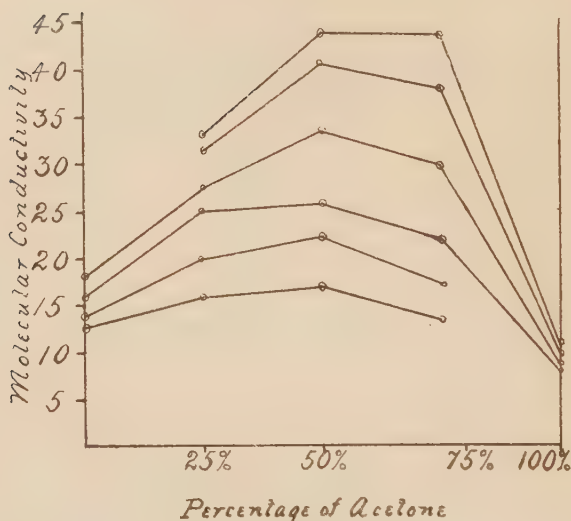


Fig. VII.

values for calcium nitrate in these mixtures, obtained by Jones and Carroll,¹ with the corresponding values for the silver salt which had been obtained by Jones and Bassett, it is seen

¹ Am. Chem. Journ., 32, 521 (1904).

that in mixtures of ethyl alcohol with water the conductivity curves for both salts are of the same form, showing no marked minimum, but exhibiting a tendency towards one in the 75 per

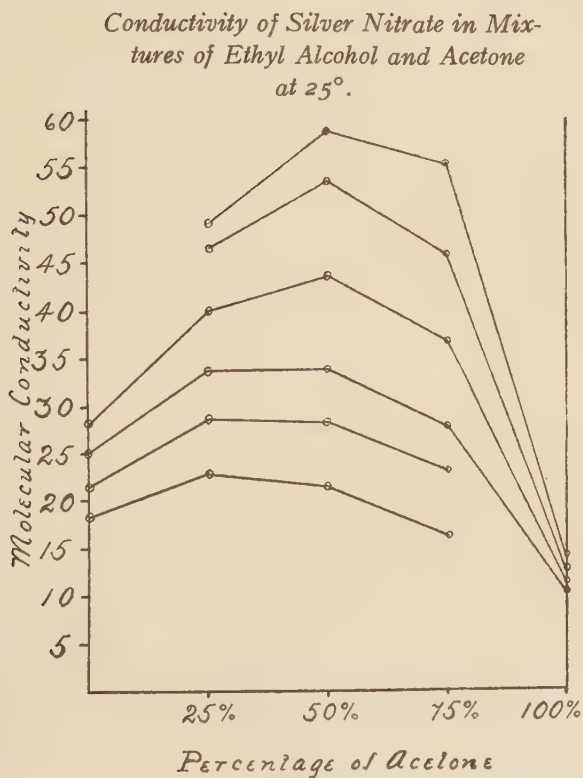


Fig. VIII.

cent alcohol mixture. In mixtures of methyl alcohol with water, however, while silver nitrate gives a very marked minimum in the 50 per cent mixture, the calcium salt does not.

Jones and Carroll did not work with dilutions greater than N/256, and it is quite possible that more dilute solutions would show a minimum.

II. Migration Velocity.

Apparatus.—The apparatus used in this investigation for the determination of the relative velocities of the ions of silver nitrate was devised by Jones and Bassett.¹ It is a modification of the form Mather² devised while working with Jones. The two outer limbs (Plate I) are 20 cm. long and 2 cm. in diameter and are connected 3 cm. below the stoppers, by a U-tube 1.5 cm. in diameter. Each arm of the U-tube is 10 cm. long, and at the center of it is a stop-cock of large bore (1 cm.). Into the electrodes, made of disks of pure silver, is riveted a short piece of stout platinum wire, which is then sealed into thick-walled glass tubes of 2 mm. bore. The exposed end of the platinum wire on the under side of the electrode was covered with fusion glass. The tubes carrying the electrodes are forced through holes bored into the ground-glass stoppers, which close the upper ends of the limbs of the apparatus. They are held firmly in place by pieces of rubber tubing. To prevent the solution from coming in contact with this rubber tubing, rings or flanges are blown on the glass tubes at the place where they enter the stopper, and are ground with carborundum to fit tightly into the holes in the stopper. To the limbs of the apparatus, just below the stoppers, are attached small, graduated tubes, 3 mm. in diameter, extending outward and upward. It was found, especially with alcohol and acetone solutions, that when the apparatus was placed in the 25° bath, a small quantity of gas always collected under the stopper and forced out some of the liquid through the side tubes. To prevent loss of solution from this source, the capacity of the side tubes was increased by attaching to them, by means of short pieces of thick rubber tubing, glass tubes of the same diameter with bulbs blown in them. An ordinary straight calcium chloride tube of small size answers the purpose very well.

¹ Am. Chem. Journ., **32**, 429 (1904).

² *Ibid.*, **26**, 473 (1901).

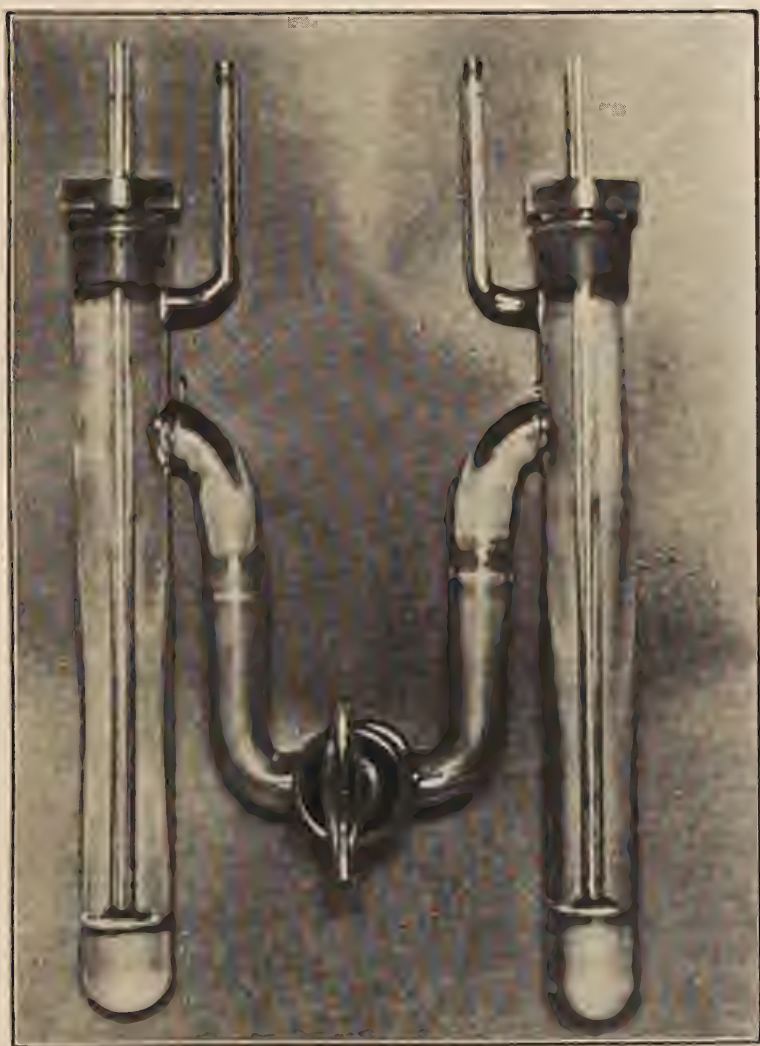


PLATE I

Electrical connection is made with the electrodes through the platinum wires riveted into them by filling the tubes which carry them with mercury.

The advantages of this form of apparatus are evident. It is easily made and handled. It is perfectly symmetrical, so that either side can be used as cathode chamber. All danger of diffusion is done away with and no membrane is necessary. The stoppers being at the top, there can be no leakage, its comparatively large capacity, about 130 cc., which may be very accurately determined, making it possible to work with large quantities of solution. By means of the small side tubes the liquid in both arms can be very accurately leveled and, finally, the stop-cock at the center of the U-tube makes it possible to separate completely the cathode and anode solutions, and to rinse out the two sides as thoroughly as may be desired. By making the bore of the stop-cock sufficiently large, the resistance offered to the current is not materially increased.

The constant temperature bath was also constructed on the same general principles as that of Jones and Bassett.¹ A wooden box, 24 inches long, 14 inches wide and 10 inches deep, is lined to within half an inch of the top with thick, galvanized iron. On one side, 1.5 inches from the top, is a heavy, movable shelf, which serves to hold the voltmeters. On the opposite side are wire hooks so arranged that, when the migration velocity apparatus is hung on them the bottom of the stoppers is level with the shelf. A section of the wooden bottom, 14 inches square, is removed and the contents of the bath can thus be heated by means of a small flame. The box is filled to the level of the shelf with water, which is kept at a uniform temperature by a small stirrer, driven by a hot-air motor. The bath proved very effective, being easily kept to within 0°.1 of the desired temperature. For measurements at 0°, the bath was filled with finely crushed ice, moistened with water, and the pieces of apparatus packed into the ice as tightly as possible. With a bath of these dimensions, 3 determinations can easily be carried out simultaneously.

The current used was always measured by means of a silver

¹ Am. Chem. Journ., 32, 430 (1904).

voltameter. On a copper disk at the bottom of a weighing bottle was placed a platinum crucible, nearly filled with a 0.1 N solution of silver nitrate. Into this solution the anode, a bar of pure silver, was dipped by forcing it through a rubber stopper which served to close the weighing bottle. The anode was wrapped in a linen bag to prevent any detached particles from falling into the crucible. Connection with the circuit was established through copper wires soldered to the disk and the silver anode.

The binding posts on the bath, used to make electrical connection with the migration velocity apparatus and the voltameters, were placed on blocks of hard rubber, and in all the wiring special precautions were taken to prevent any leakage of current. Only heavily insulated copper wire was used, and at no point was it allowed to touch the bath, being held in position by porcelain insulators. Wherever two wires were placed near each other, they were further insulated by slipping a piece of rubber tubing over them.

Migration Velocity Measurements.—All the solutions used in this work were made up approximately 0.02 N, their exact concentration being determined by titration with a solution of ammonium sulphocyanate, which had been standardized in the manner described under "conductivity measurements."

Before every experiment the crucibles of the voltameters were treated with boiling nitric acid, fused acid potassium sulphate and boiling water. They were then heated to redness and weighed. After such treatment the silver was always deposited in a very adherent form, and could easily be washed without danger of loss. At the conclusion of the experiment the crucibles were rinsed out, allowed to stand over night full of distilled water, again rinsed out, dried from 30–60 minutes at 110°–115° and cooled in a desiccator.

To determine the capacity of each arm of the migration velocity apparatus, the stoppers were placed in position, the stop-cock closed, and each side filled from a burette to the zero mark on the small side tubes. To effect this, the burette was provided with a long, slender false tip, which could reach to the bottom of the side tubes.

To fill the apparatus with the solution to be electrolyzed, both stoppers were placed in position and one of the side tubes closed with a Bunsen valve. The other was connected by a piece of rubber tubing to a glass tube passing through a two-holed stopper to the bottom of the flask containing the solution. Through the other hole of the stopper passed a short glass tube connected with a soda lime U-tube. The end of the soda lime tube nearest the flask was covered with filter paper. By blowing through this tube, the solution could be forced over into the apparatus. The side tube was closed with a second Bunsen valve, the apparatus placed in the bath, and the current passed through the solution. The electrolysis was allowed to proceed till a sufficient amount of silver had been deposited in the voltameter, usually from 0.5–0.1 gram. The liquid in both arms was then carefully leveled, the stop-cock turned, and the cathode and anode solutions filtered through glass wool into 250 cc. measuring flasks and diluted nearly to the mark with the water used to rinse out the apparatus. After standing several hours, usually over night, the solutions were diluted to exactly 250 cc., and 100 cc. portions were titrated for their silver contents. Knowing the concentration of the solution before the electrolysis, the capacity of each arm of the apparatus, the amount of silver in the cathode solution after the electrolysis, and the amount of silver deposited in the voltameter, the relative migration velocity a of the anion was calculated from the equation

$$a = \frac{\text{loss of silver on cathode side}}{\text{silver deposited in voltameter}}$$

To determine whether there had been any loss of silver by deposition of the peroxide on the anode, or from impurities in the electrodes, the anode solutions were also titrated.

Two different currents were used : one of 72 volts, furnished by a battery of storage cells, and one of 110 volts, supplied from the University power house. The current of lower voltage gave uniformly better results. The silver was usually deposited in beautiful needles on the cathode but, in some cases, especially where the current density was relatively high, the

deposit was more or less dark and of a spongy character. A thin covering of silver peroxide was generally deposited on the anode, and the analysis of the solution after the electrolysis usually showed that there had been a loss of from 0.5–1.0 per cent of silver. Some of the solutions offered a very great resistance to the passage of the current, and the electrolysis had to be continued from 12–20 hours. As it was impracticable, when working at 25° , to let the electrolysis proceed over night, it was attempted to use the city current of 220 volts which, however, was subject to rapid and irregular fluctuations all the way from 180–250 volts, but all such attempts were unsuccessful. The silver came down on the cathode in a very unsatisfactory form; there was a considerable deposition of peroxide on the anode, with a loss of silver of from 5–10 per cent, and the values obtained for the transport numbers from duplicate experiments did not show satisfactory agreement.

The acetone and alcohol solutions attacked, to a slight extent, the grease used to lubricate the stoppers and stop-cock, as was shown by the faint turbidity produced on diluting with water, but this source of error was not sufficient to affect the results materially.

The current never exceeded 0.005 ampere, and in some cases was as low as 0.001 ampere.

In the following tables, m_1 = the concentration of the solution before the electrolysis, expressed in fractions of gram-molecular weights of the salt contained in one liter of the solution; m_2 = concentration of the cathode solution after electrolysis; v = weight of silver in grams, deposited in the voltameter; and a = the transport number of the anion.

Table XXVI.—Relative Velocity of the Anion of Silver Nitrate in Water at 0° .

m_1 .	m_2 .	v .	a .
0.01999	0.01499	0.0657	0.563
0.01999	0.01464	0.0679	0.562
0.01984	0.01194	0.1014	0.557
0.01999	0.01488	0.0647	0.541

Table XXVII.—*Relative Velocity of the Anion of Silver Nitrate in Water at 0°, as Determined by Different Observers.*

m_1 .	a .	
0.1	0.5409	(Mather)
0.102	0.5628	(Jones and Bassett)
0.025	0.5377	(Mather)
0.025	0.5383	(Loeb and Nernst)
0.02	0.555	(Jones and Rouiller)

The value that we obtained is higher than that given by Mather, and by Loeb and Nernst for solutions of about the same concentration, while Jones and Bassett found, with a 0.1 N solution, a value higher than our own for the more dilute solution.

Table XXVIII.—*Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Methyl Alcohol Mixture at 0°.*

m_1 .	m_2 .	v .	a .
0.02036	0.01545	0.0671	0.546
0.02036	0.01573	0.0607	0.544
0.02030	0.01540	0.0628	0.549
0.02030	0.01551	0.0656	0.532
0.02030	0.01496	0.0703	0.541

Table XXIX.—*Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Methyl Alcohol Mixture at 0°.*

m_1 .	m_2 .	v .	a .
0.02079	0.01784	0.0399	0.541
0.02079	0.01741	0.0418	0.576
0.02069	0.01753	0.0420	0.551
0.02069	0.01723	0.0437	0.564

Table XXX.—*Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Methyl Alcohol Mixture at 0°.*

m_1 .	m_2 .	v .	a .
0.02016	0.01379	0.0848	0.514
0.02016	0.01561	0.0763	0.536

Table XXXI.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 0°.

m_1 .	m_2 .	v .	a .
0.02001	0.01483	0.0632	0.562
0.02001	0.01521	0.0629	0.559
0.02001	0.01479	0.0662	0.563

Table XXXII.—Relative Velocity of the Anion of Silver Nitrate in Water at 25°.

m_1 .	m_2 .	v .	a .
0.01999	0.01073	0.1211	0.544
0.01999	0.01128	0.1202	0.536
0.01999	0.01070	0.1155	0.543
0.02003	0.01069	0.1194	0.539

For the sake of comparison, the following table has been prepared :

Table XXXIII.—Relative Velocity of the Anion of Silver Nitrate in Water at Various Temperatures, as Determined by Different Observers.

t .	m .	a .	
11°.2	2.22	0.468	(Hittorf)
19°	2.02	0.478	"
18°.4	1.09	0.495	"
18°.8	0.87	0.510	"
75°-97°	0.49-0.64 ¹	0.513	(Bein)
9°.6-19°.2	0.39-0.024	0.5256	(Hittorf)
	0.18-0.27	0.520	(Wiedemann ²)
13°-15°	0.17 ¹	0.525	(Bein)
20°	0.104	0.528	(Loeb and Nernst)
29°.1	0.1	0.5317	(Mather)
47°.4-47°.7	0.1	0.5279	"
25°	0.1	0.5285	(Jones and Bassett)
26°	0.0521	0.524	(Loeb and Nernst)
18°-19°	0.033-0.0047	0.529	(Jahn)
26°	0.025	0.5223	(Loeb and Nernst)
45°	0.025	0.5246	(Mather)
25°	0.020	0.540	(Jones and Rouiller)
15°	0.01891	0.531	(Kistiakowsky)
26°	0.0105	0.5235	(Loeb and Nernst)

¹ Only a rough approximation; Bein expresses the concentration of his solutions in terms of percentages of silver, but does not give the specific gravity of the solutions.

² Wiedemann does not give the temperature at which he worked.

The value for the transport number, as this table shows, increases with the dilution. The value that we obtained is considerably higher than that found by other observers.

Table XXXIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Methyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02002	0.01449	0.0753	0.522
0.02002	0.01436	0.0788	0.531
0.02002	0.01356	0.0817	0.534

Table XXXV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Methyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02080	0.01548	0.0709	0.534
0.02080	0.01590	0.0683	0.531
0.02080	0.01498	0.0735	0.534

Table XXXVI.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Methyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02012	0.01410	0.0755	0.566
0.02012	0.01424	0.0758	0.572
0.02012	0.01382	0.0775	0.549

Table XXXVII.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol at 25°.

m_1 .	m_2 .	v .	a .
0.02031	0.01498	0.0653	0.581
0.02031	0.01410	0.0800	0.577
0.02031	0.01402	0.0759	0.559

Table XXXVIII.—*Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol, as Determined by Different Observers.*

<i>t.</i>	<i>m.</i>	<i>a.</i>	
		0.533	(Campetti ¹)
25°	0.0093	0.523	(Carrara)
25°	0.10	0.5797	(Jones and Bassett)
25°	0.02	0.572	(Jones and Rouiller)

The results obtained both by Jones and Bassett and by ourselves, are considerably higher than the values given by the two Italian chemists.

Table XXXIX.—*Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of These Solvents.*

<i>t.</i>	Percentage of Methyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.542	0.559	0.525	0.561
25°	0.540	0.529	0.533	0.562	0.572

The determinations of Jones and Bassett, working with 0.1 N solutions in mixtures of water and ethyl alcohol are given in the following table :

Table XL.—*Relative Velocity of the Anion of Silver Nitrate in Water, Methyl Alcohol and Mixtures of These Solvents, as Determined by Jones and Bassett.*

<i>t.</i>	Percentage of Methyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.5628	0.5379	0.5299	0.5673	0.5871
25°	0.5285	0.5538	0.6010	0.5902	0.5797

The values in Table XXXIX. are plotted as curves in Fig. IX. A study of this figure shows that at 0°, the addition of 25 per cent of alcohol to the solution produces a fall in the relative velocity of the anion, but as the proportion of alcohol is increased the value for the transport number of the $\overline{\text{NO}}_3$ ion

¹ Campetti's original paper was not available, and the abstract in the *Z. physik. Chem.* gives neither temperature nor concentration.

again increases. A still further addition of alcohol again produces a depression in the curve, while in pure alcohol the relative velocity of the anion reaches a maximum value. A similar succession of rises and falls in the curve for the transport number was observed by Goldberger¹ for barium chloride, in mixtures of water and ethyl alcohol. With 0.1 N solutions of silver nitrate, Jones and Bassett obtained a pronounced minimum in the 50 per cent methyl alcohol mixture. At 25° the curve shows that the addition of alcohol produces a slight low-

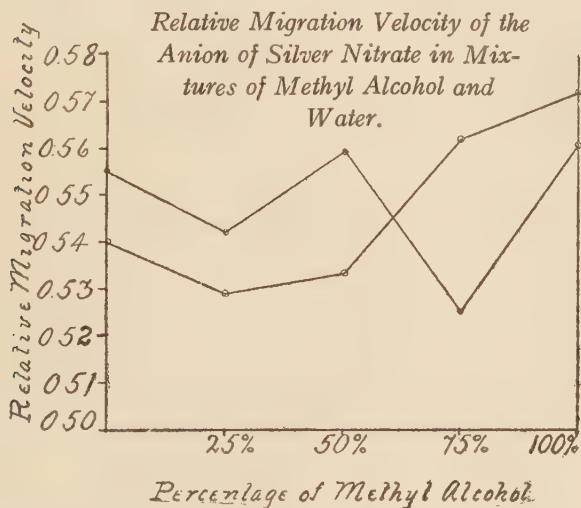


Fig. IX.

ering of the transport number, until the proportion of alcohol is raised to about 50 per cent. Further addition of alcohol produces a rapid increase in the relative velocity of the anion. Jones and Bassett, on the other hand, find that for the 0.1 N solution there is a sharp maximum in the 50 per cent mixture. A comparison of Tables XXXIX. and XL. shows that in solutions of different concentration the effect of the solvent on the migration velocities of the two ions is widely different.

¹ Roth : Z. physik. Chem., **42**, 209 (1903).

Table XLI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02042	0.01605	0.0569	0.543
0.02042	0.01654	0.0527	0.537
0.02046	0.01427	0.0843	0.534
0.02046	0.01342	0.0925	0.543
0.02042	0.01582	0.0582	0.564

Table XLII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02073	0.01777	0.0369	0.549
0.02073	0.01810	0.0358	0.537
0.02073	0.01799	0.0361	0.541

Table XLIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02052	0.01573	0.0588	0.576
0.02052	0.01593	0.0588	0.570
0.02052	0.01540	0.0616	0.593

Table XLIV.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 0°.

m_1 .	m_2 .	v .	a .
0.02000	0.01569	0.0487	0.625
0.02000	0.01587	0.0494	0.610
0.02000	0.01542	0.0519	0.627

Table XLV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Ethyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02064	0.01450	0.0820	0.528
0.02064	0.01467	0.0821	0.535
0.02064	0.01409	0.0821	0.545
0.01980	0.01556	0.0536	0.532
0.01980	0.01609	0.0530	0.517
0.01980	0.01589	0.0538	0.516

Table XLVI.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Ethyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02089	0.01590	0.0662	0.536
0.02089	0.01633	0.0649	0.521
0.02089	0.01581	0.0654	0.524

Table XLVII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Ethyl Alcohol Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02063	0.01603	0.0583	0.560
0.02063	0.01622	0.0579	0.563
0.02063	0.01600	0.0576	0.553

Table XLVIII.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at 25°.

m_1 .	m_2 .	v .	a .
0.02001	0.01717	0.0328	0.616
0.02001	0.01691	0.0364	0.633
0.02001	0.01672	0.0372	0.598

Table XLIX.—Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol at Various Temperatures, as Determined by Different Observers.

t .	m .	a .	
3°.8–5°	0.150	0.573	(Hittorf)
20°	0.108	0.594	(Mather)
25°	0.076–0.101	0.5988	(Jones and Bassett)
25°	0.020	0.616	(Rouiller)

In ethyl alcohol also, as this table shows, the velocity of the anion increases with the dilution.

Table L.—Relative Velocity of the Anion of Silver Nitrate in Water, Ethyl Alcohol and Mixtures of These Solvents.

	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.544	0.542	0.580	0.621
25°	0.540	0.529	0.527	0.559	0.616

As Table L. and Fig. X. show, at both 0° and 25° the relative velocity of the anion, in mixtures of ethyl alcohol with water, decreases slightly as the proportion of alcohol is increased, but reaches a minimum in the 50 per cent mixture.

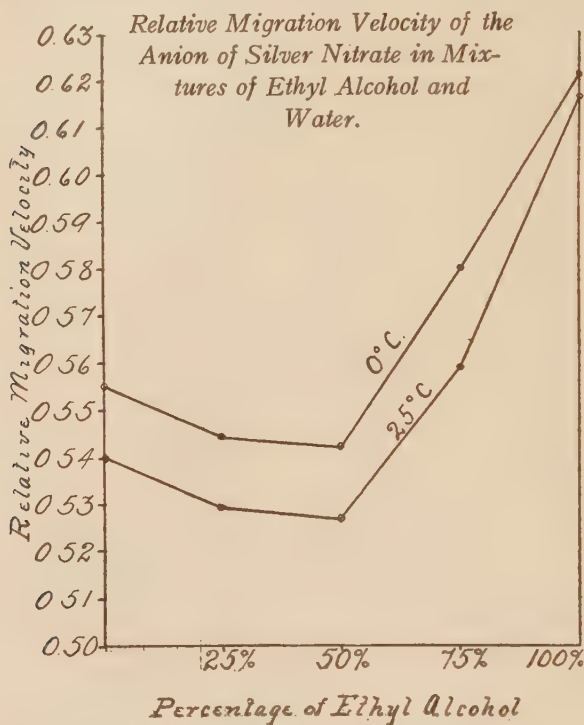


Fig. X.

From this point, increasing quantities of alcohol produce a very rapid rise in the relative velocity of the NO_3^- ion. With increasing temperature the two ions, in all these mixtures, tend to move with velocities that are more nearly equal.

Table LI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture at 0° .

m_1 .	m_2 .	v .	a .
0.02061	0.01565	0.0677	0.537
0.02061	0.01534	0.0706	0.533

Table LII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02090	0.01601	0.0647	0.552
0.02090	0.01549	0.0688	0.561

Table LIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02082	0.01598	0.0617	0.575
0.02082	0.01558	0.0647	0.579

It was found that the most concentrated solution of silver nitrate in acetone, that could be prepared by long-continued shaking of the salt with the liquid at room temperature, contained less than 0.01 gram-molecular weight of the salt to the liter. With such dilute solutions it was impracticable to make a determination of the transport number.

Table LIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Water—25 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02061	0.01301	0.1023	0.528
0.02061	0.01275	0.1098	0.530
0.02061	0.01169	0.1139	0.528

Table LV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Water—50 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02110	0.01270	0.1106	0.540
0.02110	0.01301	0.1109	0.540
0.02110	0.01248	0.1092	0.543

Table LVI.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Water—75 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02100	0.01517	0.0713	0.581
0.02100	0.01567	0.0706	0.559
0.02100	0.01518	0.0702	0.571

Table LVII.—*Relative Velocity of the Anion of Silver Nitrate in Water, Acetone and Mixtures of These Solvents.*

<i>t.</i>	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.555	0.535	0.556	0.577	. .
25°	0.540	0.529	0.541	0.570	. .

The values in Table LVII. are plotted as curves in Fig. XI. There is a pronounced minimum in the 25 per cent acetone

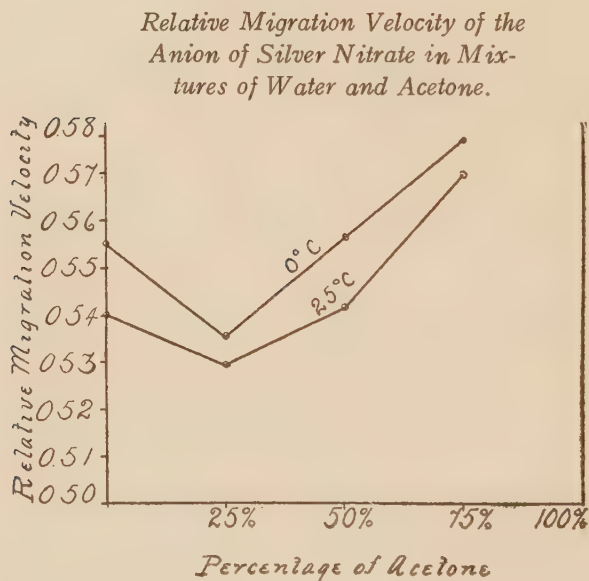


Fig. XI.

mixture. As in the mixtures with ethyl alcohol and water, the difference between the velocities of the anion and cation decreases with rise in temperature.

Table LVIII.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02004	0.01105	0.1139	0.576
0.02004	0.01023	0.1192	0.587

Table LIX.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Ethyl Alcohol Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.01996	0.01407	0.0718	0.599
0.01996	0.01376	0.0755	0.583

Table LX.—Relative Velocity of the Anion of Silver Nitrate in Methyl and Ethyl Alcohols and Mixtures of These Solvents.

t .	Percentage of Ethyl Alcohol.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.561	0.581	0.591	. .	0.621

The relative velocity of the anion in mixtures of methyl and ethyl alcohol, increases uniformly with the proportion of ethyl alcohol. This is entirely analogous to the results obtained in measuring the conductivities of solutions in mixtures of the two alcohols.

Table LXI.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02036	0.01084	0.1304	0.533
0.02036	0.01006	0.1378	0.536

Table LXII.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02038	0.01312	0.0934	0.569
0.02038	0.01276	0.0966	0.563

Table LXIII.—Relative Velocity of the Anion of Silver Nitrate in a 25 Per Cent Methyl Alcohol—75 Per Cent Acetone Mixture at 0°.

m_1 .	m_2 .	v .	a .
0.02037	0.01539	0.0580	0.627
0.02037	0.01498	0.0620	0.620

Table LXIV.—Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Methyl Alcohol—25 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02020	0.01541	0.0583	0.584
0.02020	0.01545	0.0599	0.588
0.02020	0.01505	0.0617	0.563

Table LXV.—Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Methyl Alcohol—50 Per Cent Acetone Mixture at 25°.

m_1 .	m_2 .	v .	a .
0.02028	0.01549	0.0556	0.613
0.02028	0.01570	0.0534	0.634
0.02028	0.01578	0.0498	0.609

Table LXVI.—Relative Velocity of the Anion of Silver Nitrate in Methyl Alcohol, Acetone and Mixtures of These Solvents.

t .	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.561	0.534	0.566	0.623	. .
25°	0.572	0.578	0.619	. .	. .

Table LXVI. (Fig. XII.) shows that in methyl alcohol and acetone the transport number of the anion has a minimum

*Relative Migration Velocity of the Anion
of Silver Nitrate in Mixtures of Methyl
Alcohol and Acetone.*

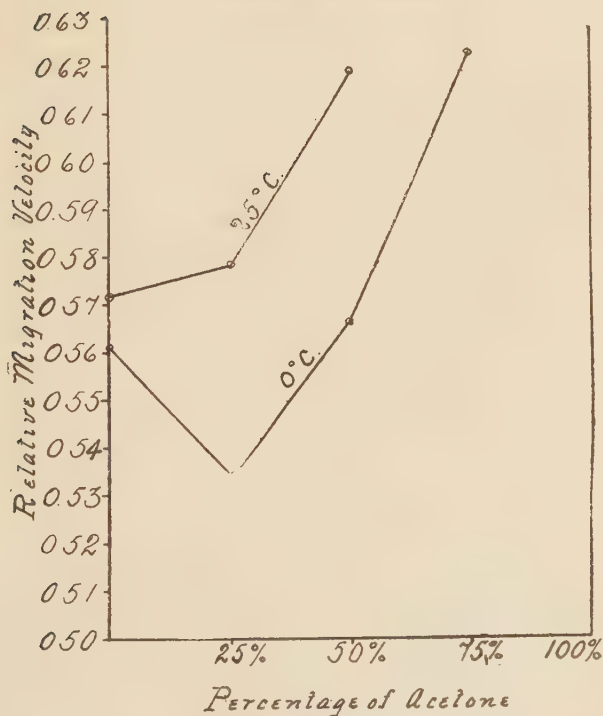


Fig. XII.

value, at 0°, in the mixture containing 25 per cent of acetone. At 25° the minimum has disappeared. It is interesting to note that in these mixtures the relative velocity of the anion increases with rise in temperature.

Table LXVII.—*Relative Velocity of the Anion of Silver Nitrate in a 75 Per Cent Ethyl Alcohol—25 Per Cent Acetone Mixture at 0°.*

m_1 .	m_2 .	v .	a .
0.02003	0.01421	0.0730	0.564
0.02003	0.01454	0.0690	0.580

Table LXVIII.—*Relative Velocity of the Anion of Silver Nitrate in a 50 Per Cent Ethyl Alcohol—50 Per Cent Acetone Mixture at 0°.*

m_1 .	m_2 .	v .	a .
0.02001	0.01451	0.0643	0.585
0.02001	0.01493	0.0634	0.586
0.02001	0.01461	0.0665	0.579

Table LXIX.—*Relative Velocity of the Anion of Silver Nitrate in Ethyl Alcohol, Acetone and Mixtures of These Solvents.*

i .	Percentage of Acetone.				
	0 per cent.	25 per cent.	50 per cent.	75 per cent.	100 per cent.
0°	0.621	0.572	0.583		.

In ethyl alcohol and acetone, there is a pronounced minimum in the relative velocity of the anion in the mixture containing 25 per cent of acetone.

PART III.

Discussion of Results.

Changes produced in the relative migration velocities, or transport numbers of the ions of an electrolyte, by varying the nature of the solvent, may be due to three causes:

1. Owing to some property peculiar to one of the ions, its velocity may be influenced by the solvent more than the velocity of the ion with the opposite charge.

2. Complex ions may be formed, which are more or less dissociated, according to the nature of the solvent, into simpler ions.

3. The ions may combine with the solvent itself.

That ions do combine with the solvent in many cases has been established, especially by the work of Jones and his pupils in this laboratory. But, if this is to affect the *relative*

velocities of the positive and negative ions, the solvent must combine with only one ion, or *different* quantities of it must combine with anion and cation, respectively. This, in substance, is the view proposed by Jones and also by Kohlrausch.¹ "About every ion there moves an atmosphere of the solvent, whose dimensions are determined by the individual characteristics of the ions. . . . The electrolytic resistance is a frictional resistance that increases with the dimensions of the atmosphere. The direct action between the ion and the outer portion of the solvent, diminishes as the atmosphere becomes of greater thickness. . . . For a very sluggish ion there will be only the friction of water against water, and the electrolytic resistance will have the same temperature coefficient as the viscosity of the water, provided the atmosphere itself does not change its dimensions with the temperature. If, however, the atmosphere becomes, for example, smaller with increasing temperature, the temperature gradient of the conductivity might be greater than that of the fluidity. According to observations now at hand, this would seem to be the case for the slowest moving, univalent ion, Li."

It has been attempted to show experimentally that the solvent does, in some cases, unite with only one, or in greater quantities with one ion. Thus, Oppermann,² by electrolyzing silver acetate in a mixture of acetic acid and water, concluded that the ion CH_3COO^- carries with it 6 more molecules of water than the silver. Working along the same lines with silver nitrate in methyl alcohol and water, Lobry de Bruyn³ obtained negative results. Morgan and Kanolt,⁴ using essentially the apparatus devised by Jones and Bassett, thought they found that in mixtures of water and ethyl alcohol the cation of silver nitrate carries along with it 1 molecule of water more than the anion. Their experimental work is, however, far from convincing, and their erroneous statement that the results of Jones do not show whether it is the free ions that are combined with solvent molecules, could easily have been

¹ P. Roy. Soc., **71**, 338 (1903).

² Dissertation, Göttingen, 1901.

³ Rec. Trav. Chim., **22**, 430 (1903).

⁴ J. Am. Chem. Soc., **27**, 572 (1906).

avoided by simply reading the recent papers of Jones and Bassett.¹ In pyridine and water the silver ion carries, according to them, pyridine to the cathode.

The fact that the transport numbers of the ions of many simple binary electrolytes, where the possibility of the formation of complex ions is very doubtful, change with the dilution until they reach a constant value, is in harmony with the Kohlrausch view. That there is preferential combination of the solvent with one of the ions we cannot prove directly for pure solvents, but, if we arrange electrolytes in groups, according to the power of forming hydrates in solution, as determined by Jones and his co-workers, we find that, in general, *the power of forming hydrates is, in some way, dependent on the nature of the cation and more or less independent of the anion.* Thus, sodium, potassium and ammonium salts fall in the group showing the least tendency to form hydrates. Iron and aluminium salts form complex hydrates, while calcium, strontium and magnesium salts are intermediate between them and the alkali salts. If we compare these facts with the phenomena exhibited by transport numbers, we find that the relative velocities of the cations of salts with small power of hydration are practically independent of the concentration, while the transport numbers of such ions as calcium, strontium and magnesium, increase with the dilution. It is true that this may be due largely to the presence of complex ions in the more concentrated solutions, but the relative velocity of the cation of lithium chloride which, alone of the alkali chlorides crystallizes with water of crystallization, also increases considerably with the dilution. This can hardly be due to the presence of complex ions in the more concentrated solutions.

The data for transport numbers in non-aqueous solvents, at different dilutions, are too meagre to show whether this is true for other solvents than water. That it holds for silver nitrate in pyridine and acetonitrile has been shown by Schlundt.

Silver nitrate in water is a striking exception. The velocity of the anion increases with the dilution. It should be noted, however, that the nitrates of sodium and potassium exhibit

¹ Am. Chem. Journ., **33**, 583 (1905); **34**, 346 (1906).

the same phenomena, although not quite so strikingly. The relative velocities of the cations of these salts decrease slightly with the dilution. It would seem, therefore, that in these salts it is the anion that is combined with the larger amount of the solvent.

Rise in temperature, as shown by Jones, would have a tendency to break up hydrates in solution. It has been found experimentally that, in most cases, raising the temperature increases the relative velocity of the slower ion.

That the relative ionic velocities for certain electrolytes are affected by the presence of complex ions, at least in the more concentrated solutions, is generally accepted. Reference need only be made to the classical case of cadmium iodide, which was first studied by Hittorf, and has since been the subject of a large number of investigations. As there is little probability that silver nitrate forms complex ions, this point will not be discussed in the present paper.

Finally, that the fluidity of the solvent affects the migration velocities is true beyond doubt, but how it affects the *relative* velocities we cannot as yet say. It is, of course, impossible to obtain solutions containing ions of only one kind and measure their viscosities, so that we are unable to determine, for any electrolyte in a given solvent, whether the friction of ion against solvent is greater for the cation than for the anion, or *vice versa*. In the present state of our knowledge, the influence of size and configuration on relative ionic velocities is also unknown. It may be stated that, in the course of this investigation, although working with solvents having such widely different fluidities as water, methyl and ethyl alcohols and acetone, it has not been possible to trace any connection between the transport numbers of the same ion and the fluidities of the solvents. This can be seen from the table given below. The values for the fluidities of the solvents are taken from the work of Jones and Bingham (see Table LXX.).

That there is any connection between the influence of the solvent on transport numbers and the nature of the charge carried by the ion, is very improbable. If there were any such connection, the influence of one solvent on different ions

with the same kind of charge, other things being equal, would always be in the same direction ; in other words, it would always increase the relative velocity of the anion, or *vice versa*. Here again, the lack of data for transport numbers of suffi-

Table LXX.—*Relative Migration Velocity of the Anion of Silver, Nitrate in Water, Methyl and Ethyl Alcohols and Acetone, with the Fluidity of These Solvents, at 0° and 25°.*

Solvent.	0°.		25°.	
	Fluidity.	Transport No.	Fluidity.	Transport No.
Water	56.24	0.555	112.3	0.540
Methyl alcohol	122.20	0.561	176.7	0.572
Ethyl alcohol	53.88	0.621	90.35	0.616
Acetone	244.10	>0.620	308.9	>0.620

ciently dilute solutions in non-aqueous solvents, makes it impossible to draw any general conclusion as to the existence or non-existence of such a relation.

Since, from the increase with the dilution, of the relative velocity of the anion of silver nitrate in water, it would seem that the negative ion is combined with a greater quantity of the solvent, we should expect the addition to the solution of some "dehydrating agent," such as alcohol, would have the same effect as an increase in concentration in the water solution ; in other words, *a decrease in the relative velocity of the anion*. That this is true for ethyl alcohol up to the 50 per cent mixture, and that the increase is slightly more marked at 0° than at the higher temperature, as would be expected, is shown by Fig. X. As the relative velocity of the anion in pure alcohol is much larger than in water, increasing amounts of alcohol will tend to retard the cation, and beyond the 50 per cent mixture the effects of decreasing hydration are entirely masked and the relative velocity of the anion increases rapidly.

In this connection, attention should be called to the work of Lobry de Bruyn and Jungius¹ and of Bruni and Manuelli,² who have shown, by cryoscopic methods, that certain hydrated salts, when dissolved in organic solvents, retain part of their water of crystallization.

¹ Rec. Trav. Chim., **22**, 421 (1903).

² Z. Elek. Chem., **10**, 601 (1904).

Looking at Fig. IX., it will be seen that what has been said for ethyl alcohol and water is true of methyl alcohol and water at 25°. But the increase in the relative velocity of the cation with the addition of alcohol to the solvent is not so marked, and the influence in the opposite direction of increasing amounts of alcohol, already manifests itself in the 50 per cent mixture. The curve for the transport number of the anion at 0° shows a minimum in the 25 per cent mixture, but beyond the 50 per cent mixture it is abnormal. No explanation for this can as yet be offered.

Although we have no experimental evidence that proves directly that in water and acetone the anion of silver nitrate is more "hydrated" than the cation, yet, by analogy with the alcohol and water mixtures, we should expect this to be the case. A study of Fig. XI. will show that in these mixtures there is at first a decrease, which is more marked at the lower temperature, in the relative velocity of the anion as alcohol is added to the solution. The turning point in the direction of the curve, however, is already reached in the mixture containing only 25 per cent of acetone. This is what we should expect if the effect of pure acetone on the relative ionic velocities of the anion and cation is taken into account. Although we have been unable to determine the transport numbers in pure acetone, all measurements made with mixtures containing increasing quantities of it tend to show that in the pure solvent the relative velocity of the anion is greater even than in pure ethyl alcohol. It is not surprising, therefore, that the addition of more than 25 per cent to an aqueous solution should entirely offset the effect of decreasing hydration and produce an increase in the relative velocity of the anion.

The results for mixtures of methyl alcohol and acetone are of the same nature. As with mixtures of water and acetone, we have no direct evidence that one ion carries more of one of the constituents of the solvent mixture than the ion of opposite charge. But a study of Fig. XII. makes it seem probable that the anion carries methyl alcohol with itself. At 0°, as the proportion of acetone is increased, the value for the transport number of the anion passes through a pronounced mini-

imum in the 25 per cent mixture. At 25° there is no actual minimum, but up to the 25 per cent mixture there is practically no increase in the relative velocity of the anion. It is interesting to note that in these mixtures, although the transport number of the anion is less at 0° than at 25° , the influence of the solvent is, as usual, more pronounced at the lower temperature.

The data for mixtures of ethyl alcohol and acetone (Table LXIX.) are too fragmentary to make any generalization possible, yet they show that the relative velocity of the anion passes through a minimum in the mixture containing 25 per cent of acetone.

The striking parallelism exhibited by calcium and silver nitrates, when their conductivity phenomena in binary mixtures of acetone with water and methyl and ethyl alcohols are compared, is very interesting in view of certain relations observed by Jones and Bingham between the conductivities of potassium iodide, calcium nitrate and lithium nitrate, and the migration velocities of the cations of these salts. Our conductivity measurements confirm the conclusions reached by them, but as it has no direct bearing on this investigation, reference only is made to their work.¹

Summary.

1. I have measured the conductivity of silver nitrate in acetone, and in binary mixtures of this solvent with water, methyl alcohol and ethyl alcohol. The results were of the same general nature as those obtained by Jones and Bingham for calcium nitrate.

2. The transport number of the anion of silver nitrate in binary mixtures of water, methyl alcohol, ethyl alcohol and acetone has been determined at two temperatures, 0° and 25° .

3. That increase in temperature, in general, increases the velocity of the slower ion has been confirmed. Solutions in mixtures of methyl alcohol with acetone, in pure methyl alcohol and in a 75 per cent mixture of methyl alcohol with water are exceptions.

¹ Amer. Chem. Journ., **34**, 481 (1905).

4. It has been shown that the nature of the solvent very materially affects relative migration velocities. That this is due to varying degrees of combination of the solvent with one of the ions, as compared with the ion of opposite charge, is very probable.

BIOGRAPHY.

The author of this dissertation, Charles August Rouiller, was born in Paraje, Socorro Co., New Mexico, on June 10th, 1883.

He received his preparatory instruction at the Goss Military Institute, Albuquerque, New Mexico, and in the fall of 1899, entered Leland Stanford Junior University. He received the degree of Bachelor of Arts from that University in January, 1903, and spent the next half-year there in graduate work.

In the fall of 1903 he entered Johns Hopkins University as a graduate student in chemistry. His subordinate subjects were physical chemistry and physics.

